CERTIFICATE OF TRANSLATION

I, Xun XU, 435 Guiping Road Shanghai 200233, CHINA, hereby certify that to the best of my knowledge and belief, the attached English translation is a true translation, made by me and for which I accept responsibility, of the CN Application No. **200310116687.7**, filed in China on **November 27, 2003**, in the names of WANG, Shoufeng, and CHEN, Zhaoran.

This 16 day of May, 2006

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PROCESS FOR DISTILLATION AND DECARBONIZATION OF OIL SHALE SPECIES USING FLUIDIZED BED

FIELD OF THE INVENTION

The present invention relates to a process for distillation and decarbonization of oil shale species using fluidized bed. In particular, the present invention belongs to the coal chemical engineering field, directing to research and development for a process for dry distillation and decarbonization of oil shale species using a fluidized bed.

BACKGROUND OF THE INVENTION

The oil shale, a kind of sedimentary rock, contains abundant organics. A ton of oil shale can produce at least 38L of shale oil, that is to say, oil shale contains 2-30% of shale oil. Recently, the studies around the world have shown that oil shale is a rich resource, but it has not been well utilized. It is estimated that about 3,000 billion barrels of raw oil are stored in the oil shale, and the raw oil is called as shale oil, among which only less than 200 billion barrels are utilized by the prior art. Presently, it is much more expensive to extract oil from the oil shale than to purchase raw oil. Due to the problems in the exploitation technology, the fund and the environment, the oil extracted from the oil shale cannot completely replace the raw oil in the market of petrochemical fuel in the next dozens of years. Additionally, the inorganics (also known as the parent material of the oil shale) in the oil shale from different places of production varies a lot, and the most of the inorganics (parent material) is silicon-aluminum-oxide. After the organic matter and the carbon are removed, the parent material with high content of silicon and aluminum and low level of other impurities can be used as the carrier of catalyst, while other parent material with high content of impurities can be used as construction material.

Typically, the oil shale and coal gangue are associated minerals of coal, both of which are piled as garbage after being dug out with the coal. The piled oil shale or coal gangue occupies the land, and furthermore, it is easy to autoignite.

Brown coal, peat coal, peat cube, etc. also comprise many organics, and therefore, after dry distillation, they produce coal tar which is similar to heavy crude. The coal gangue and the oil shale have many in common, but the coal gangue contains only a few organics and much carbon.

The existing industrialized technology for processing oil shale is to grind the oil shale to be used as fuel for power generation or boiler furnace. The developing and developed technology for extracting oil shale comprises the methods using solid heat carrier and that

using gas heat carrier, and the methods for producing oil shale organic compound fertilizer, producing cement, firing building brick, etc. The main disadvantages of the technology using solid heat carrier to extract oil shale are the severe wear the device, the short cycle of the production, and the difficulty of energy recovery. The technology using gas heat carrier consumes much energy and causes a certain dust pollution. In 50-60s of last century, the development and application of oil shale processing technique in our country was very active, and a great number of industrial experiments and test production were conducted for dry distillation technique of oil shale and coal, and, many researches for a technique for dry distillation of coal using fluidized bed were conducted. However, the processing for oil shale is nearly forgotten due to the discovery of petroleum.

Recently, because of the emergence of the petroleum crisis, the efforts to find new resources are extremely active. The solar energy, hydrogen energy, wind energy, tide energy and nuclear energy, etc. are under development or partly used. The technique for the extraction of shale oil from oil shale and the liquidization of coal is regarded as a technique which is mostly possible to supplement and replace petroleum energy.

No similar patents relating to the dry distillation and decarbonization of oil shale species using fluidized bed are searched. Most of the prior arts relate to one-step methods of fluidizing combustion or recycling fluidizing combustion, which seldom utilize the parent material of oil shale. Chinese Patent Application CN 91102884 discloses a process for removing and transforming the minerals in the oil shale, and the main content thereof is to pretreatthe oil shale with strong acid or alkali to improve its combustion performance and the chemical engineering availability. The main disadvantages of this patent application lie in that the use of strong acid and alkali during the process increases the danger of operation and causes some pollution to the environment, furthermore, it is merely a pretreatment process. Chinese Patent Application CN 93102071 discloses a method for producing combustible gas from the inferior solid fuel such as the oil shale or other analogues. The technology in this patent application employs boiling bed process, the main disadvantages of which lie in that all of the shale oils are pyrolyzed into combustible gas, and therefore the aromatic compounds in the shale oil cannot be sufficiently recovered to give aromatic product with high added value or raw materials for petroleum chemical industry.

To completely utilize the aromatic compounds in the shale oil, the mature technique for processing petroleum, i.e. fluidizing, catalyzing and cracking technique, is used to conduct fluidizing distillation and decarbonization of oil shale species, to effectively employ various sources in the oil shale. Thus, we finish a process for

distillation and decarbonization of oil shale species using fluidized bed.

SUMMARY OF INVENTION

The principle of the present invention is the principle of reacting by using fluidized bed. The shale oil contained in powdered oil shale in fluidizing condition is gasified by using high temperature dry gas and/or high temperature stream as heat carrier and fluidizing medium, meanwhile, dry gas dissolves some organics in oil shale, that is, fluidizing, dry distillating and deoiling. The powder which has removed shale oil is fluidized by high temperature air under oxygen-rich condition. The carbon in oil shale is combusted, i.e. fluidizing decarbonization. A energy recovery system(i.e. the system of the flue gas turbine and the residue heat boiler)is set for the high temperature produced in the decarbonization reactor. After energy recovery and purification by removing compounds such as sulfide and nitrogen compounds, the flue gas is discharged.

The key of the present invention is the technique for grinding oil shale species, the technique for dry distillating the oil shale and pyrolizing the heavy shale oil simultaneously completed in the same reactor, and the technique for combusting carbon under oxygen-rich condition

The main advantages of the present invention are: The fluidizing dry distillating of the oil shale and pyrolysis of the heavy shale oil are simultaneously completed in the same reactor, and the deoiled oil shale is decarbonized in another reactor. The shale oil can be used to produce products with high added values, such as aromatics, light oil for chemical industry and fuel gas, to make sufficient use of substances derived from the oil shale. The exhaust gas containing sulfur and nitrogen can be discharged after purification and energy recovery, therefore, it hardly causes environmental pollution. Upon using the system of energy recovery, the total energy of the system according to the present invention is excessive, and the excess energy can be delivered outside. The oil shale only needs physically grinding, without chemical treatment.

The processing scheme of the present invention is described briefly as follows: The large block of oil shale is physically grinded, with the size distribution of the grinded particle controlled to make the particle size be 0-1000 micrometers, more preferably 50-800 micrometers, and be normal distribution. The powdered oil shale is delivered into the dry distillation reactor, and the powdered oil shale is fluidizing distilled with steam and/or dry gas. Meanwhile, the heavy shale oil is delivered into

the dry distillation reactor and pyrolyzed at a high temperature. After the oil gas produced in the dry distillation reactor is cooled down by condensation, the gaseous hydrocarbon compounds are separated therefrom, and then the different fractions are fractionated from the gaseous hydrocarbon compounds; gasoline and diesel oil fractions may be further processed to give gasoline and diesel oil mixture composition, light oil for chemical industry, fuel oil, aromatic products, etc; and the heavy oil fraction may be further thermally cracked to produce light oil, or it can be directly used to produce coal pitch. The distilled oil shale powder from the dry distillation reactor is delivered into the decarbonization reactor, into which adequate hot air is introduced and where the carbon is combusted to be completely removed. The flue gas is discharged after purification and energy recovery. The powder is stored after being cooled down, wherein the carbon content thereof is less than 0.5%, and used as different products dependent on its physical and chemical properties.

The fluidized bed reactor of the present invention includes reactor riser, batch-type fluidization kettle reactor, bubbling-type fluidized bed reactor, and moving bed reactor. The most preferred one is reactor riser. There may be 2-4, preferably 2, reactor risers mounted depending on the nature of the raw material and the purpose product. The top of the reactor riser has cyclone separator of 3 levels, in order to maximize the reduction of the fume discharge.

The grinding of the oil shale according to the present invention includes the breaking of the large block and the grinding. Large blocks of oil shale are broken into crushed aggregates with particle size of less than 5 cm, preferably less than 3 cm, by crushing machinery. These crushed aggregates are grinded into 50-300 mm powder by a fine grinding machinery such as Raymond mill and pneumatic crusher. The present invention can be used to process solids containing carbon such as coal gangue. The processing scheme for processing the oil-containing coal is identical to that for processing oil shale. The deoiled and decarbonized solid substances are utilized comprehensively according to their different chemical compositions. Deoiling reactor may be omitted in the case of processing the coal gangue.

The reaction condition for the fluidized bed reactor according to the present invention is: the operation pressure of 0.1-0.2 MPa, the operation temperature of 400-800°C, and the ratio of gas to solid of 1.0-20.0: 1(v/v).

The heavy shale oil according to the present invention comprises the shale oil fraction of above 350°C, the fraction of 350-500°C, and/or the fraction therebetween. The heavy shale oil may be thermally cracked in the dry distillation reactor, or be used

to produce coal pitch, preservative coatings, the fuel for firing the porcelain, etc.

The principle of the patent is illustrated in Figure 1.

DESCRIPTION OF DRAWINGS

The meanings of the reference signs in Figure 1 are as follows:

1-block oil shale, 2-two-stage crasher, 3-oil shale powder, 4-dry distillation reactor, 5-oil gas, 6-high temperature dry gas, 7-heavy shale oil, 8-deoiled oil shale, 9-flue gas, 10-decarbonization reactor, 11-high temperature air, 12-deoiled and decarbonized oil shale, 13-fractionating tower, 14-tower top gas, 15-gasoline fraction, 16-diesel oil fraction, 17-coal pitch, 18-discharged dry gas, 19-liquefied gas, 20-gas separation tank, 21-condensate oil.

Now, the present invention will be illustrated in detail together with the flow process chart 1.

The block oil shale 1 is grinded into powdered oil shale 3 by two-stage crasher 2, and then delivered into the dry distillation reactor 4. The high temperature dry gas 6 and heavy shale oil 7 entered into the dry distillation reactor 4 from the bottom thereof, and they are deoiled by dry distillating and thermally cracked, respectively. The deoiled oil shale 8 is delivered into the decarbonization reactor 10. The high temperature air 11 enters the decarbonization reactor 10 from the bottom thereof, and completely burns the residue carbon in the oil shale in fluidizing condition. The flue gas 9 is discharged from the top and released after purification and heat recovery. The deoiled and decarbonized oil shale 12 is discharged from the upper part and stored after being cooled down. The oil gas 5 discharged through the top of the dry distillation reactor, after being cooled down, is delivered into fractionating tower 13, where the oil gas 5 is fractionated into tower top gas 14, gasoline fraction 15, diesel oil fraction 16, heavy shale oil 7, and coal pitch 17. In the gas separation tank 20, the fractionating tower gas 14 is separated into dry gas 6, discharged dry gas 18, liquefied gas 19 and condensate oil 21.

Now, the invention is further illustrated by the following examples.

DETAILED DESCRIPTION OF INVENTION

Example

The oil shale from a certain place contains 10% of oil, up to 85% of kaolin (mainly aluminum oxide and silicon oxide), and 5% of carbon. Since the parent material of the oil shale is substantially the kaolin with high quality, kaolin products

with high quality were obtained by deoiling and decarbonization in this patent. Some light oil for chemical industry, diesel oil admixture composition, liquefied gas, coal pitch, a small amount of aromatic products were simultaneously obtained.

The process flow was two fluidized bed reactors in the form of reactor riser, one of which was a dry distillation reactor, the other was a decarbonization reactor. The heavy shale oil of above 400°C was introduced into the dry distillation reactor and thermally cracked. There was a precipitator settled on the top of the reactor riser, which had two levels of cyclone separators, and a third level of cyclone separator before the flue gas entering the energy recovery part.

The process conditions were as follows:

1) The dry distillation reactor

the reaction pressure of 0.15 MPa, the reaction temperature of 500°C, the ratio of gas to solid of 4.0:1 (v/v).

2) The decarbonization reactor

the reaction pressure of 0.15 MPa, the reaction temperature of 680°C, the ratio of gas to solid of 4.0:1 (v/v).

3) Crashing

The oil shale was broken into crushed aggregates with the diameter of less than 3 cm by roller crusher, then grinded into 50-400 mm powder by high pressure milling machine.

4) Fractionating

A normal-reduced process was used.

The oil shale was first grinded into 50-400 mm powder by two-stage grinding, then delivered by the dry air into the dry distillation reactor. The oil in the oil shale was gasified by dry distillating under the conditions described above, and meanwhile, the heavy shale oil is thermally cracked. The deoiled oil shale was delivered into the reactor riser for decarbonization by steam. The carbon in the oil shale was completely combusted under the conditions described above to become kaolin products (with carbon content of 0.2%) after being cooled down. The flue gas produced during the carbon combustion was energy-recovered by a flue machine, and then washed by saturated white lime water before discharge. The oil gas from the top of the dry distillation reactor was cooled down by condensation, then delivered into the fractionating tower and distilled, then cut. The distribution of the products was: the dry gas and liquefied gas: 20%; 65-180°C light oil for chemical industry: 40%; 180-350°C diesel oil admixture composition: 20%; heavy shale oil of above 350°C:

20%, wherein 10% of the heavy shale oil of above 350°C was delivered into the dry distillation reactor for thermal cracking, and the rest part was used as coal pitch products.

After the processing by the technique in this patent, the final products included: kaolin with high quality, liquefied gas, light oil for chemical industry, diesel oil admixture compositions, and a small amount of coal pitch.

In comparison with the current fluidizing combustion method, the method according to the present invention mainly has the following advantages: more varieties of products obtained, the parent material of the oil shale being of good use, the high operation flexibility of the reactor riser process, and the smaller amount of fume discharge.

What is claimed is:

1. A process for dry distillation and decarbonization of oil shale species using fluidized bed, comprising: deoiling the powdered oil shale species by dry distillating in the fluidized bed reactor, combusting carbon under oxygen-rich condition, thereby obtaining liquid oil products, gaseous hydrocarbons and solid products.

2. The process according to claim 1, wherein the powdered oil shale species are obtained by at least two-stage grinding, and the particle diameter thereof is preferably 0-1000μm, more preferably 50-800μm; and the two-stage grinding can be two-stage mechanical grinding and/or one-stage mechanical grinding plus one-stage gas stream grinding or shaking grinding.

3. The process according to claim 1, wherein the oil shale species include oil shale, coal, coal gangue, peat coal and peat cube, and the setting of dry distillation reactor and fractionating tower is dependent on the oil content of raw oil.

4. The process according to claim 1, wherein the fluidized bed reactor can be reactor riser, batch-type fluidization kettle reactor, bubbling-type fluidized bed reactor, and moving bed reactor, preferably the reactor riser; the number of the reactor riser can be 2-4 dependent on the properties of raw materials and the purpose products, preferably 2; and the top of the reactor riser has cyclone separator of at least two levels in order to maximize the reduction of the fume discharge.

5. The process according to claim 1, wherein the dry distillating and deoiling can be performed by using high temperature dry gas and/or high temperature stream as a medium for delivering the powdered oil shale species and a heat carrier; the heavy shale oil can be introduced and thermally cracked during dry distillating; and the operation temperature of the dry distillation reactor is 400-800°C.

6. The process according to claim 1, wherein the combustion of carbon under oxygen-rich condition refers to a technique of combusting carbon under excess thermal air, and the ratio of the gas to solid is preferably 1.0-20.0:1 V/V.

Abstract

The present invention discloses a process for dry distillation and decarbonization of oil shale species using fluidized bed. The shale oil contained in oil shale having certain size distribution in fluidizing condition is gasified by using high temperature dry gas and/or high temperature stream as heat carrier and fluidizing medium, meanwhile, dry gas dissolves some organics in oil shale, that is, fluidizing, dry distillating and deoiling. The powder which has removed shale oil is fluidized by high temperature air under oxygen-rich condition. The carbon in oil shale is combusted, i.e. fluidizing decarbonization. The deoiled and decarbonized oil shale parent material can be used as kaolin, construction material, etc. The resultant shale oil can be used to produce aromatic hydrocarbon products with high added values, light oil for chemical industry and fuel gas, to make sufficient use of substances derived from the oil shale. The exhaust gas containing sulfur and nitrogen can be discharged after purification, therefore, it hardly causes environmental pollution. The oil shale only needs physically grinding, without chemical treatment.

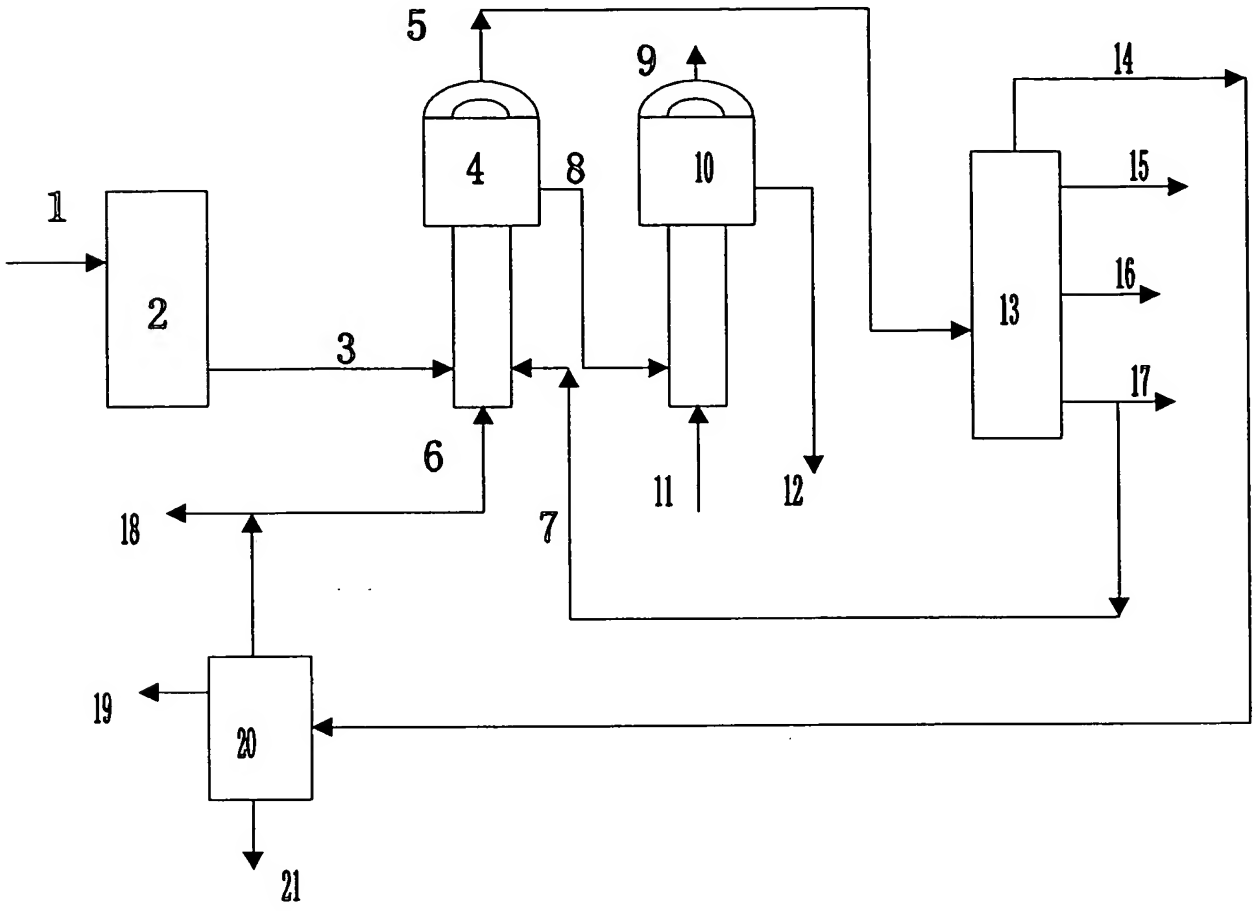

Fig. 1